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TITLE: EMULSIONS FOR FUEL CELLS

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EMULSIONS FOR FUEL CELLS

BACKGROUND

In typical proton exchange membrane (PEM) fuel cells, a proton conducting membrane is sandwiched between the anode and cathode and is often called a membrane electrode assembly (MEA). The membrane serves multiple purposes. It acts as an insulator for electron conduction, while conducting positive and negative charges. It also provides a solid support for the catalytic layers and separates the fuel from the oxidant feed, so that mixing or crossover does not take place.

The fuel may be delivered to the electrode in the gaseous form, for example molecular hydrogen, or liquid form, for instance methanol or formic acid dissolved in water. Oxygen, however, typically enters the cell in gaseous form, as a component of air or as pure oxygen. Due to the chemical nature of the membrane, this gives rise to logistical problems that lower cell performance. When both the fuel and the oxidant feeds are gaseous, the gasses need to be humidified so as not to dry out the PEM. If the PEM dries out, the cell performance drops considerably. In addition, the PEM needs to be kept at low temperatures, whereas the catalyst at the cathode and anode perform best at high temperatures. A cooling apparatus for the membrane is thus often needed.

Problems arise with liquid fuels as well. For instance, when methanol is introduced as an aqueous based fuel, the membrane is slightly permeable to it and crossover of the fuel to the cathode takes place. The crossover causes consumption of fuel at the cathode without production of electricity, and results in a mixed potential at the cathode, causing a considerable drop in potential.

Laminar flow fuel cells avoid the need for a PEM. In this type of cell, parallel laminar flow between two streams of liquid creates an interface between the streams, which replaces the PEM or salt bridge of conventional devices. When the first stream, containing an oxidizer, comes into contact with the first electrode, and the second stream, containing the fuel, comes into contact with the second electrode, a current is produced, while charge migration from the anode to the cathode occurs through the interface. This cell design

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minimizes crossover by maximizing consumption of the fuel before it diffuses into the oxidant stream.

However, in laminar flow fuel cells both fuel and oxidant are delivered in liquid form, and both the fuel and oxidant fluids must be proton conductive. This limits the applicability of oxygen as the oxidant, because this gas is characterized by a low solubility in water and aqueous solutions of electrolytes.

SUMMARY

In a first aspect, the invention provides a method for transporting gas, whereby the gas is dissolved in an emulsion comprising a fluorinated hydrocarbon, a surfactant and an aqueous electrolyte with a pH of at most 4 or at least 9. The emulsion then comes into contact with an electrode.

In a second aspect, the invention provides emulsions for delivering gas and ions to an electrode, comprising a fluorinated hydrocarbon, a surfactant, and an aqueous electrolyte with a pH of at most 4 or at least 9.

In a third aspect, the invention provides a fuel cell for the generation of electricity, comprising an anode and a cathode wherein at least one of the anode and the cathode is in contact with an emulsion comprising a fluorinated solvent, a surfactant and an aqueous electrolyte with a pH of at most 4 or at least 9.

DESCRIPTION OF THE FIGURES

FIG. 1 depicts the cyclic voltamogram of Example 1.

FIG. 2 depicts the current voltage plot of Example 1.

FIG. 3 depicts the current voltage plot of Example 3.

FIG. 4 depicts the current voltage plot of Example 4.

FIG. 5 depicts the current voltage plot of Example 5.

FIG. 6 shows a cross-sectional schematic illustration of a PEM fuel cell.

FIG. 7 shows a cross-sectional schematic illustration of a laminar flow fuel cell.

DETAILED DESCRIPTION

The performance of both PEM and laminar flow cells would benefit from transporting oxygen to the cathode with a fluid having a very low affinity for the fuel and a high affinity for oxygen and carbon dioxide. In a PEM cell, crossover could be minimized, while the fluid would remove heat from the cathode in a more efficient fashion than a gaseous stream. In a laminar flow cell, oxygen dissolved in the liquid could be used as the oxidant at high concentrations, while fuel crossover could be further reduced.

Fluorinated solvents, such as fluorinated hydrocarbons (viz., perfluorinated fluids such as perfluorodecalin available from F2 Chemicals Ltd., Preston, UK) have a very high affinity for oxygen and carbon dioxide and have been successfully used in respiration-type fluids for medicinal applications, such as artificial blood (Clark et al., Journal of Fluorine Chemistry, Vol. 9, pp. 137-146, 1977). However, fluorinated solvents by themselves would not be good choices as they are very strong insulators with a low dielectric constant and not good at charge separation or ionic conduction.

The present invention provides for liquid-phase delivery and removal of a gas to an electrode, and in particular of oxygen to the cathode of a fuel cell, and CO_2 from its anode, by making use of fluorinated solvent emulsions. These fluids are also proton conductive and maintain the flow of positive charges to the cathode, or OH^- conductive and maintain the flow of negative charges to the anode. Furthermore, they are usually inert to electrocatalysts, and have a high capacity for carbon dioxide. Fuel crossover is also minimized, and the cooling effect exerted by these emulsion reduces the need for active cooling.

The invention includes emulsions of fluorinated solvents in aqueous electrolytes, the compositions including a fluorinated solvent, an aqueous electrolyte and a surfactant. These emulsions combine the gas transporting capabilities of fluorinated hydrocarbons with the charge conductivity of aqueous electrolytes. Alternatively, the aqueous phase may be emulsified in the fluorinated solvents, yielding a reverse phase micellar structure, where the fluorinated solvent is the continuous phase.

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Fluorinated solvents, including hydrochlorofluorocarbons, perfluorocarbons, hydrofluorocarbons, hydrofluoroethers, hydrofluoroesters, and fluorosylanes, are characterized by a low chemical reactivity and a high affinity for oxygen.

Preferred fluorinated solvents include: $(C_nF_{2n+1})Si(OCH_3)_3$; $(C_nF_{2n+1})_2Si(OCH_3)_2$; $(C_nF_{2n+1})CH_2OC(O)CH_3$; $CF_3[OCF_2CF_2]_nOCF_3$; $CF_3[OCF_2CF_2]_nOCF_2Cl$; $CF_3[OCF_2CF_2]_nOCF_2Br$; $CF_3[OCF_2CF_2]_nCF_2H$; $CF_3[OCF_2CF_2]_nF$; $CF_3[OCF_2CF_2]_nCl$; $CF_3[OCF_2CF_2]_nBr$; $CF_3[OCF_2CF_2]_nH$; $CF_3CF_2[OCF_2CF_2]_nF$; $CF_3CF_2[OCF_2CF_2]_nCl$; $CF_3CF_2[OCF_2CF_2]_nBr$; $CF_3CF_2[OCF_2CF_2]_nH$; $CF_3CHF[OCF_2CF_2]_nF$; $CF_3CHF[OCF_2CF_2]_nCl$; $CF_3CHF[OCF_2CF_2]_nBr$; $CF_3CHF[OCF_2CF_2]_nH$; $CF_3CHF[OCF_2CF(CF_3)]_nF$; $(CF_3)_2CF(CF_2)_nF$; $(CF_3)_2CF(CF_2)_nCl$; $(CF_3)_2CFO(CF_2)_nBr$; $(CF_3)_2CFO(CF_2)_nH$; $(CF_3)_2CFO(CF_2)_nF$; $(CF_3)_2CFO(CF_2)_nCl$; $(CF_3)_2CFO(CF_2)_nBr$; $(CF_3)_2CFO(CF_2)_nH$; C_nF_{2n+2}; $CF_3(CF_2)_nCl$; $CF_3(CF_2)_nHCF_3(CF_2)_nBr$; $N(C_nF_{2n+1})_3$ wherein n is 1 to 20; $C_6F_mH_{6-m}$, $C_6F_mCl_{6-m}$, $C_6F_mBr_{6-m}$, $C_6F_m(CF_3)_{6-m}$, wherein m is 1 to 6; and mixtures thereof.

Particularly preferred fluorinated solvents include: $CF_3(CF_2)_7Br$; $(CF_3)_2CF(CF_2)_4Cl$; $(CF_3)_2CFO(CF_2)_6F$; perfluorobutyltetrahydrofuran; perfluoropropyltetrahydropyran; C_8F_{18}; $CF_3CFBrCF_2Br$; $(CF_3)_2CF(CF_2)_4Br$; $[(CF_3)_2CFOCF_2CF_2]_2$; C_9F_{20}; C_6F_6; $CF_3CHF[OCF_2CF(CF_3)]_3F$; $(CF_3)_2CF(CF_2)_6Cl$; $C_{10}F_{16}$; $CF_3CHF[OCF_2CF(CF_3)]_4F$; perfluorotetrahydrodicyclopentadiene; $[(CF_3)_2CFO(CF_2)_4]_2$; perfluorodecalin; $CF_3CHF[OCF_2CF(CF_3)]_5F$; perfluorodimethyladamantane; $N(C_4F_9)_3$; perfluoromethyldecalin; $C_6H_4(CF_3)_2$; and $CF_3CHF[OCF_2CF(CF_3)]_9F$.

Preferably, the fluorinated solvent is inert to the materials in the fuel cell. For example, when the cathode is platinum, as is the case in most fuel cells, and methanol or formic acid is the fuel, the use of perfluorodecaline (PFD) is particularly indicated. This fluorinated solvent is inert to the catalyst and has minimal affinity for either fuel.

The surfactant emulsifies the fluorinated solvent in the water phase, and is preferably inert to the electrode in order not to cause poisoning. Thus, compatibility between surfactant and electrode should be determined. A simple test for this determination is as follows: a first cyclic voltamogram is run on the electrode in a test solution, followed by a second

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voltamogram in the same solution with a quantity of the surfactant. The occurrence of discrepancies between the former and the latter will reveal electrode poisoning.

Fluorinated surfactants, alone or in combination with non-fluorinated surfactants, are preferred for the emulsification of fluorinated solvents. Preferred fluorinated surfactants include: $F(CF_2CF_2)_y(CH_2CH_2O)_xH$, wherein y is 1 to 10, and x is 0 to 25; $((F(CF_2CF_2)_zCH_2CH_2)_xP(O)(ONH_4)_y$, wherein x is 1 or 2, y is 1 or 2, x + y is 3, and z is 1 to 8; $F(CF_2CF_2)_xCH_2CH_2SCH_2CH_2CO_2Li$, wherein x is 1 to 10; $F(CF_2CF_2)_xCH_2CH_2SO_3Y$, wherein x is 1 to 10, and Y is H^+ or NH_4^+. Other surfactants may be found in *Fluorinated Surfactants, Synthesis, Properties, Applications* (Eric Kissa; Marcel Dekker Publisher, 1993). For example, when the fluorinated solvent is PFD, $CF_3(CF_2)_5CH_2CH_2SO_3X$ (X = H or NH_4), commercially available as ZONYL® FS-62 (DuPont, Wilmington, DE) is a particularly preferred surfactant.

The electrolyte enhances charge conductivity of the emulsion, but should not poison the electrode. Also, a high concentration of charges improves the current from the fuel cell. For fuel cells operating in acidic conditions, acidic electrolytes such as solutions of H_2SO_4, HNO_3, $HClO_4$, H_3PO_3, H_3PO_4, HCl, HBr, HI, CH_3CO_2H, CCl_3CO_2H, CF_3CO_2H, and mixtures thereof, are preferred. For fuel cells operating in alkaline conditions, alkaline electrolytes such as solutions of LiOH, NaOH, KOH, Rb(OH), CsOH, $Mg(OH)_2$, $Ca(OH)_2$, $Sr(OH)_2$, and $Ba(OH)_2$ are mixtures thereof are preferred.

Additional electrolytes, for example inorganic salts, may be added. When PFD is the fluorinated solvent, and $CF_3(CF_2)_5CH_2CH_2SO_3X$ (X = H or NH_4) the surfactant, H_2SO_4 is a particularly preferred electrolyte.

Fluorinated solvent : aqueous electrolyte volume-to-volume ratios can vary greatly, since direct and reverse micellar structures can both act as charge conductive oxygen carriers. Preferred ratios range from 1:24 to 24:1, more preferably 3:24 to 12:24, yet more preferably 1:6 to 5:7, and most preferably from 2:9 to 4:9. The preferred amount of surfactant may vary from 0.07% to 3% by weight of the total weight of the emulsion, more preferably 0.125% to 2%, and most preferably 0.5% to 1%.

FIG. 6 shows a cross-sectional schematic illustration of a (PEM) fuel cell **2**. Fuel cell **2** includes a high surface area anode **4** that acts as a conductor, an anode catalyst **6** (typically platinum alloy), a high surface area cathode **8** that acts as a conductor, a cathode catalyst **10** (typically platinum), and a PEM **12** that serves as a solid electrolyte for the cell. The PEM **12** physically separates anode **4** and cathode **8**. Fuel in the gas and/or liquid phase is brought over the anode catalyst **6** where it is oxidized to produce protons and electrons in the case of hydrogen fuel, and protons, electrons, and carbon dioxide in the case of an alcohol fuel. The electrons flow through an external circuit **16** to the cathode **8** where air, oxygen, or another is being constantly fed. Protons produced at the anode **4** selectively diffuse through PEM **12** to cathode **8**, where oxygen is reduced in the presence of protons and electrons at cathode catalyst **10** to produce water.

In the laminar flow cell **20**, as seen in FIG. 7, both the fuel input **22** (for example an aqueous solution containing MeOH) and the oxidant input **24**, a solution containing oxygen dissolved in one of the emulsions of the invention and a proton source, are in liquid form. By pumping the two solutions into the channel **26**, parallel laminar flow induces the interface **28** that is maintained during fluid flow. Rapid proton diffusion **29** completes the circuit of the cell as protons are produced at the anode **30** and consumed at the cathode **32**. In this case, the interface **28** prevents the two solutions from mixing and allows rapid proton conduction to complete the circuit. In addition, methanol crossover is minimized by the very low affinity of the emulsion of the invention for methanol. If fuel crossover into the emulsion occurs, the emulsion is recovered, the fuel is separated and the solution may be re-circulated in the cell. Furthermore, since both liquids are excellent heat exchangers, an external cooling system is not required.

The fluids may also be used to deliver oxidant gases other than oxygen, for example N_2O and O_3. Likewise, the fluid compositions of the invention may also be used to transport fuel gases, for example H_2, to the anode.

EXAMPLES

1) Emulsions

PFD was emulsified using a mixture of $CF_3(CF_2)_5CH_2CH_2SO_3H$ and

$CF_3(CF_2)_5CH_2CH_2SO_3NH_4$ (ZONYL® FS-62, DuPont) in aqueous 0.5 M H_2SO_4 via a

ultrasonic homogenizer. The emulsion was prepared at the concentrations of PFD reported in

Table 1.

Table 1

Emulsion	Volume 0.5 M H_2SO_4 solution (mL)	Volume of PFD (mL)	Amount of ZONYL® FS-62	Volume of PFD emulsified (mL)
1A	30	0	0	0
2A	20	10	5 drops	3
3A	20	10	5 drops	10

The resulting emulsions were exposed to a Pt catalyst and were found to be inert, as

seen in the cyclic voltamogram of FIG. 1. The emulsions were then saturated with oxygen

for ½ hour and tested in a laminar flow fuel cell with formic acid as the reductant. As seen in

the current voltage plot of FIG. 2, the emulsion with the largest PFD content showed the

largest current when compared to aqueous streams that were saturated with oxygen in the

same way and introduced in the cell at the same flow rate (0.3 mL/min).

2) Concentration effects of ZONYL® FS-62 on emulsions

Emulsion experiments were performed with different concentrations of ZONYL® FS-

62 to determine the ability to emulsify and the stability of the emulsion. As can be seen from

the results of Table 2, a minimum of 0.25 wt% ZONYL® FS-62 in 20 mL 0.5 M sulfuric acid

was needed to emulsify 10 mL (1:3) of PFD under ultrasonication conditions. Higher

ZONYL® FS-62 concentrations led to better, and more stable emulsions.

Table 2

Emulsion	Volume 0.5 M H_2SO_4 solution	Volume of PFD (mL)	Amount of ZONYL® FS-62	Volume of PFD emulsified	Stability

	(mL)			(mL)	
1B	20	10	1 wt%	10	Weeks
2B	20	10	0.5 wt%	10	Days
3B	20	10	0.25 wt%	10	2-3 days
4B	20	10	0.125 wt%	3-4	0

3) PFD concentration effects on fuel cell

To test the concentration effects of the PFD in the laminar flow fuel cell, the emulsions listed in Table 3 were prepared, saturated with oxygen for ½ hour before being inserted into a laminar flow cell at a flow rate of 0.3 mL/min. As seen in the current voltage plot of FIG. 3, emulsion 3C shows the highest current profile which correlates with it having the highest oxygen content.

Table 3

Emulsion	Volume of 0.25 wt% ZONYL® in 0.5 M H_2SO_4 solution (mL)	Volume of PFD (mL)	Stability
1C	27.5	2.5	Week
2C	25	5	Days
3C	20	10	2-3 days

4) Oxygen concentration effects on fuel cell.

Emulsion 1B was exposed to oxygen in air and run through the laminar flow fuel cell. The same experiment was repeated, this time exposing the emulsion to pure oxygen. As seen in FIG. 4, the increase in oxygen concentration resulted in an increased current output, especially at lower voltages.

5) Limit of currents obtainable with the emulsions.

To find the limit of the current that could be reached with the laminar flow fuel cell, another series of emulsions were made with varying amounts of PFD, as can be seen in Table 4. All of these emulsions were stable and are assumed to have a reversed micellar structure at PFD concentrations greater than 50%. All of the emulsions were saturated with pure oxygen

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for ½ hour and run through a laminar flow fuel cell, as previously done. As seen in FIG. 5, the current for each emulsion followed nearly the same trend, although the oxygen concentration was undoubtedly increasing through the series. One possible explanation may be that some other factor, for example high resistance of the cell, was limiting the current that the cell could produce and the cell performance was no longer related to oxygen concentration. Nevertheless, these experiments proved that reverse micellar structures can also act as both oxygen carriers and proton conductors.

Table 4

Emulsion	Volume of 2 wt% ZONYL in 0.5 M H_2SO_4 solution (mL)	Volume of PFD (mL)	Stability
1D	20	10	Week
2D	17.5	12.5	Week
3D	15	15	Week
4D	12.5	17.5	Week

Other experiments have been performed with the PFC emulsions in conventional fuel cells, and the emulsions have been found to function in much the same way as in the laminar flow fuel cell. They showed no deleterious effect on this type of device, proving that the fluid may be used in conventional PEM based fuel cells as well.

6) Use of PFD-based emulsion in a PEM fuel cell (prophetic example).

In a PEM fuel cell, the anode compartment is filled with a gas transporting emulsion, and H_2 is bubbled in the emulsion. Both gas transporting emulsions are obtained by emulsifying 10 ml of PFD in 20 ml of 0.5 M sulfuric acid, with an amount of ZONYL® FS-62 equivalent to 1% of the total weight of the emulsion. The cathode compartment is also filled with a gas transporting emulsion, and O_2 is bubbled in the emulsion. The apparatus may also run on a continuous stream of oxidant and fuel solutions, for example in a laminar flow fuel cell.